Optical detrapping in solids

Morsink, Jos B. W.; Wiersma, Douwe A.

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.441620

Publication date:
1981

molecule in the supersonic beam without the need to know the various branching ratios which are necessary for obtaining the same information from excitation spectra. We are currently carrying out these measurements on DMT.

In conclusion, the efficacy of applying intracavity absorption spectroscopy to vibrationally and rotationally cold large molecules in supersonic beams has been demonstrated. Despite the low molecular density and small optical path length encountered in the jet, the absorption properties can be determined. Moreover, we feel that because of the large enhancement factor, this technique can also be used to probe forbidden transitions in a molecular beam. Further technical development, particularly with regard to increasing the resolution and extending the tuning range of the dye laser, will improve the versatility of this technique.

[a]This work was supported in part by the National Science Foundation under grant CHE79-05683.
[b]Alfred P. Sloan Fellow and Camille and Henry Dreyfus Foundation Teacher–Scholar.
[c]Contribution No. 6367.

[1]D. H. Levy, L. Wharton, and R. E. Smalley, *Chemical and Biological Applications of Lasers VII*, edited by C. B. Moore (Academic, San Francisco, 1977).
[2]A. Amirav, V. Even, and J. Jortner, Chem. Phys. 51, 31 (1980).
[3]V. Vaida and G. M. McClelland, Chem. Phys. Lett. 71, 436 (1980).
[4](a) P. Kumar, G. O. Brink, S. Spence, and H. S. Lakkaraju, Opt. Commun. 32, 129 (1980); (b) T. W. Hänsch, A. L. Schawlow, and P. E. Toschek, IEEE J. Quantum. Electron. 8, 802 (1972); (c) W. T. Hill III, R. A. Abreu, T. W. Hänsch, and A. L. Schawlow, Opt. Commun. 32, 96 (1980); (d) R. G. Bray, W. Henke, S. K. Liu, K. F. Reddy, and M. J. Berry, Chem. Phys. Lett. 47, 213 (1977); (e) V. M. Baev, T. P. Belikova, E. A. Sviridenkov, and A. F. Suchkov, Sov. Phys. JETP 47, 21 (1978); (f) G. H. Atkinson, T. N. Heimlich, and M. W. Schuyler, J. Chem. Phys. 66, 5005 (1977); (g) H. Schröder, H. J. Neusser, and E. W. Schlag, Opt. Commun. 14, 395 (1975).
[5]J. S. Shirk, T. D. Harris, and J. W. Mitchell, Anal. Chem. 52, 1701 (1980).
[6]S. J. Harris, J. Chem. Phys. 71, 4001 (1979).
[7]G. G. Asmuth, K. K. Innes, and V. A. Job (to be published).
[8]R. M. Hochstrasser, D. S. King, and A. B. Smith III, J. Am. Chem. Soc. 99, 3923 (1977).
[9]R. E. Smalley, D. H. Levy, and L. Wharton, J. Chem. Phys. 64, 3266 (1976).
[10]M. Paczkowski, R. Pierce, A. B. Smith III, and R. M. Hochstrasser, Chem. Phys. Lett. 72, 5 (1980).
[11]The enhancement factor is linear in the function $(P/P_{th})/(P-P_{th})$, as discussed in Ref. 6.

Optical detrapping in solids

Jos B.W. Morsink and Douwe A. Wiersma

Picosecond Laser and Spectroscopy Laboratory, Department of Physical Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands
(Received 2 January 1981; accepted 3 February 1981)

Trapping and detrapping processes are of prime importance in energy transport phenomena in crystals. Guest emission after host excitation,[1] even at very low guest (impurity) concentration, is the most striking feature of excitation trapping. This trapping process, which occurs through exciton motion and radiationless relaxation at the trap site, is still a subject of current interest.[2] When the trap depth (Δ) far exceeds the Debye frequency (ω_D), we speak of a deep trap, and the reverse process of detrapping is not observed. In the opposite case, where $\Delta \ll \omega_D$, we have a shallow trap and here we can easily observe the phenomenon of phonon-assisted detrapping. Harris and co-workers[3–5] have recently studied this effect in some detail in molecular solids and proposed a stochastic model for phonon-assisted detrapping.

In this communication we are concerned with *optical* (photon-assisted) detrapping. Here the excitation from a deep trap is transferred by a laser to the host exciton band.

So far, laser-induced energy transfer processes have only been observed in gases.[6,7] Jortner and Ben-Reuven,[8] however, theoretically examined laser-induced transfer in solids and suggested the possibility of observing trap–host energy transfer in molecular crystals.

In this letter we demonstrate the feasibility of such an experiment and show that the effect can be used to explore the band structure of the host–acceptor state. The system we have chosen is pentacene (PTC) in naphthalene (NT), whereby the pentacene is a deep trap ($\Delta = 14\,887$ cm^{-1}). The relevant energy diagram is shown in Fig. 1. The transfer we discuss in this report is between the lowest excited singlet state of PTC and the lowest singlet exciton band of NT.

The experiment was performed by exciting, collinearly, a PTC in NT mixed crystal by two nitrogen-pumped dye lasers. One dye laser operates at the PTC transition (16 588 vac cm^{-1}), while the other is tuned to a frequency which corresponds with the PTC trap depth Δ. Both lasers are focused in the crystal to a spot of $\sim 100\ \mu$ diameter. Under these conditions the peak power at the sample of both lasers is ~ 2 MW cm^{-2}.

 0021-9606/81/084734-02$01.00

Laser-induced transfer (linear with intensity) is observed by collecting the naphthalene emission on a photomultiplier, using appropriate filters. After pulse stretching, the signal was processed by an Apple II computer for averaging procedures. Furthermore, the transfer spectrum was corrected for the wavelength dependency of the transfer laser intensity.

Figure 2 shows a typical transfer spectrum, whereby the transfer laser is polarized parallel to the crystal a axis. The b-polarized spectrum is identical. We first note that time-resolved experiments show that the spectrum is *not* due to two-photon effects of the host crystal.[9] The sharp "spike" at 461 cm^{-1}, however, is caused by this effect and induced by the combined action of the pump and transfer laser. We further point out that the "dips" in the spectrum have been identified as the result of stimulated emission (induced by the transfer laser) in PTC.

The most surprising feature of the transfer spectrum is that even at 1.5 K it is broad and structureless. In fact, the spectrum resembles most, as shown by the dotted curve, the *density-of-states function* of the NT host singlet exciton band.[10]

This can be rationalized in the following way: In a perturbative approach to laser-induced trap-to-host energy transfer, the transfer probability per unit time $[W_{th}(E)]$, for the indicated route, can be written as

$$W_{th}(E) = \frac{2\pi}{\hbar} n(\nu_{tr}) |\langle i_t | \mu_t \cdot \hat{\epsilon} | j_t \rangle \times \langle j_t g_h | V_{th} | g_t f_h(k) \rangle|^2 \rho_{f_h}(E) \ . \quad (1)$$

Here $n(\nu_{tr})$ represents the number of photons in the field of the transfer laser polarized along $\hat{\epsilon}$. i_t, j_t, and g_t are the initial, "virtual," and ground state of the trap, while g_h and $f_h(k)$ are the ground and final (exciton) state, with wave vector k, of the host. $\rho_{f_h}(E)$ is the density of host states at the sum frequency ($E/h = \nu_p + \nu_{tr}$) of the pump and transfer laser.

When in Eq. (1), for V_{th} the intermolecular Coulomb interaction is taken and expanded in a multipole series, it is easy to show that transfer can only occur to the $k = 0$ states of the host exciton band. Furthermore,

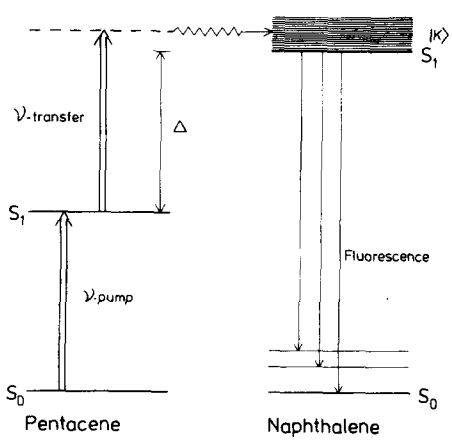

FIG. 1. Energy-level scheme of the pentacene (trap) in naphthalene (host) mixed crystal.

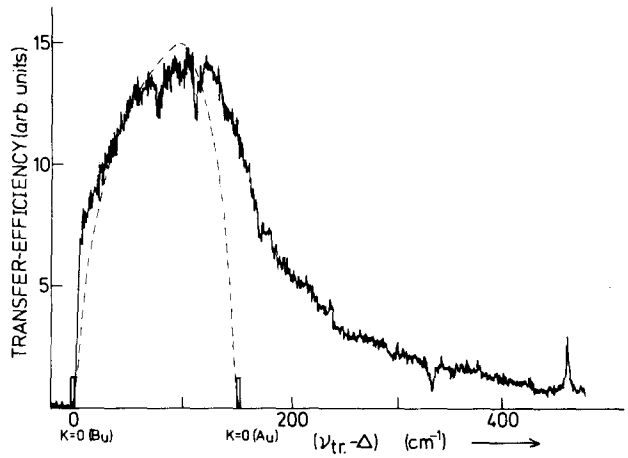

FIG. 2. Laser-induced energy transfer spectrum of pentacene in naphthalene (10^{-6} m/m).

transfer through dipole–dipole coupling in the chosen mixed crystal system is forbidden by parity selection rules. We therefore propose that laser-induced energy transfer in the PTC in NT crystal occurs through exchange. In this case, the transfer is symmetry allowed and the exciton wave vector can be generated from the trap. Consequently, transfer to *all* k states in the band should be possible. With the additional assumption that the exchange matrix element is independent of k, Eq. (1) leads to the interesting result that the transfer rate $W_{th}(E)$ should mimic $\rho_{f_h}(E)$.

We suggest that this basically explains the correspondence between the observed transfer spectrum and the density of states function of the host exciton band. The deviation at the high energy side we interpret, tentatively, as a result of exciton–phonon coupling.

In conclusion we note that laser-induced transfer spectra not only can be employed as a tool for the study of band structures of both organic and inorganic solids, but also can be used to search for hereto, spectroscopically, unidentified states.

We gratefully acknowledge the assistance of Jaap van der Giessen and Johan Kemmink in the experiments.

[1] K. W. Benz and H. C. Wolf, Z. Naturforsch. Teil A 19, 177 (1964).
[2] H. Auweter, A. Braun, U. Mayer, and D. Schmid, Z. Naturforsch. Teil A 34, 761 (1979).
[3] M. D. Fayer and C. B. Harris, Phys. Rev. B 9, 748 (1974).
[4] H. C. Brenner, J. C. Brock, M. D. Fayer, and C. B. Harris, Chem. Phys. Lett. 33, 471 (1975).
[5] M. T. Lewellyn, A. H. Zewail, and C. B. Harris, J. Chem. Phys. 63, 3687 (1975).
[6] R. W. Falcome, W. R. Green, J. C. White, J. F. Young, and S. E. Harris, Phys. Rev. A 15, 1333 (1977).
[7] P. Cahuzac and P. E. Toschek, Phys. Rev. Lett. 40, 1087 (1978).
[8] J. Jortner and A. Ben-Reuven, Chem. Phys. Lett. 41, 401 (1976).
[9] R. M. Hochstrasser and H. N. Sung, J. Chem. Phys. 66, 3276 (1977).
[10] H. K. Hong and R. Kopelman, J. Chem. Phys. 55, 724 (1971), and references therein.